FY2018 5th CREST Workshop

Towards Reproduction of Stereochemistry of Polypropylene by Using Red Moon Method

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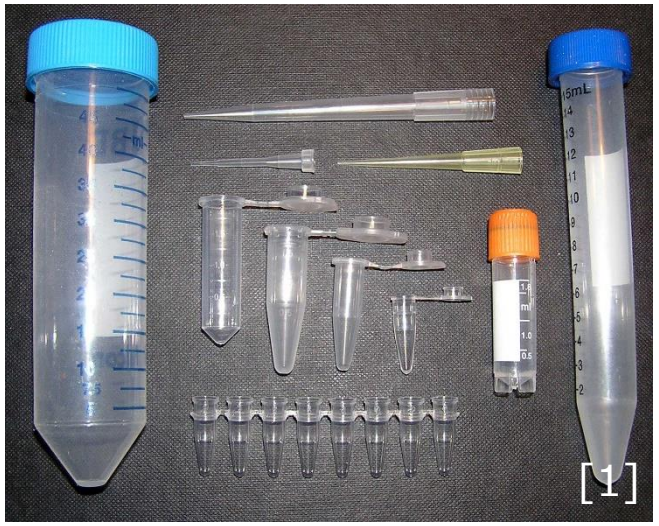
2019/03/05

Introduction: Polyolefins

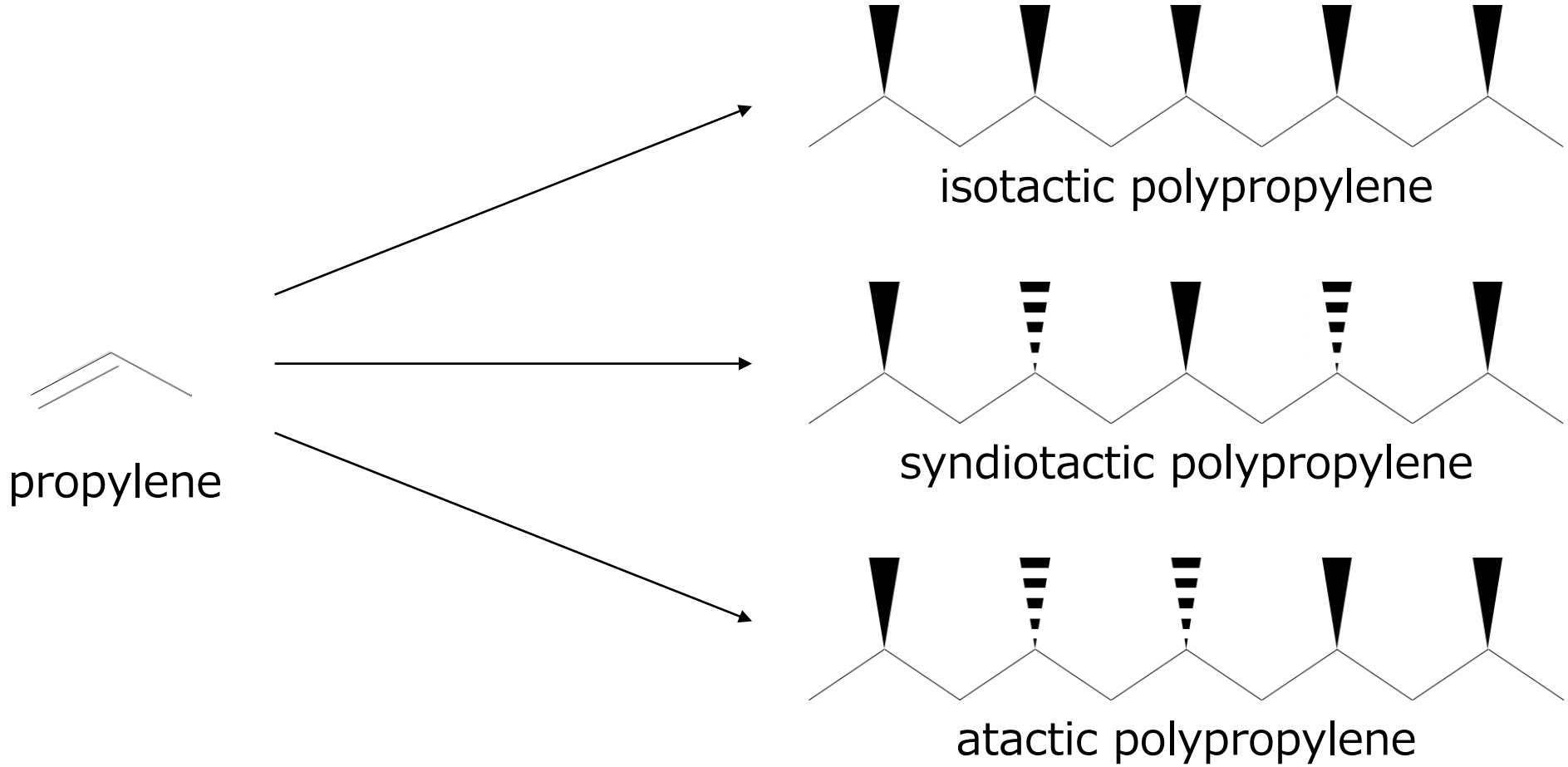
- Polyethylene
- **Polypropylene**
- Polystyrene
- Polyvinyl chloride



Global market for polypropylene
~ 5.5×10^7 t (in 2013)[1]

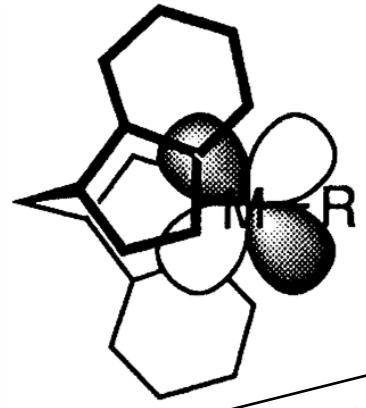
[1] https://en.wikipedia.org/wiki/Polypropylene

Introduction: Stereochemistry of Polypropylene

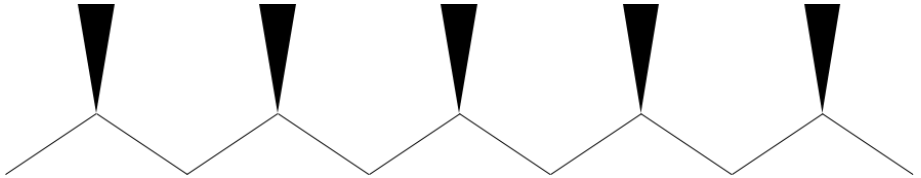


Tacticity affects the properties of polymer.
→ The control of the tacticity is important.

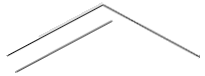
Introduction: Stereochemistry of Polypropylene



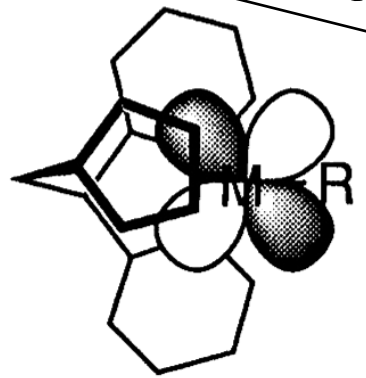
C_2 symmetric catalyst

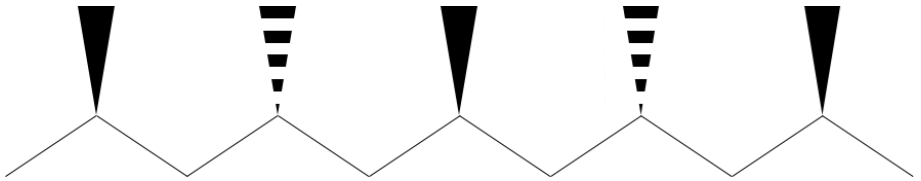


isotactic polypropylene [2,3]



C_s symmetric catalyst

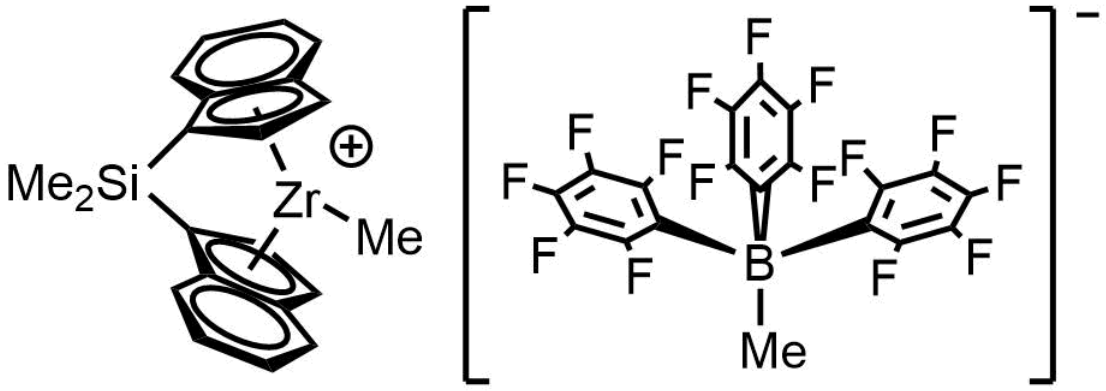




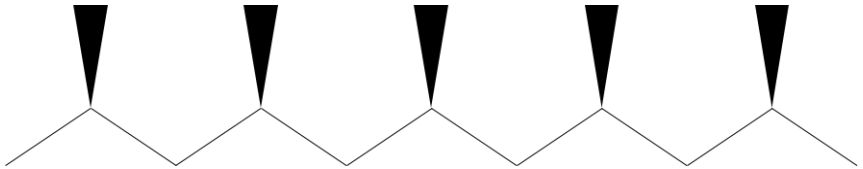
syndiotactic polypropylene [2,3]

[2] Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1996**, *15*, 766.
[3] Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1345.

Introduction: Stereochemistry of Polypropylene



produces



isotactic polypropylene.

C_2 symmetric *ansa*-zirconocene catalyst,
$[SiMe_2(Ind)_2ZrMe]^+[MeB(C_6F_5)_3]^-$ (**1**) [4]

Instantaneous and microscopic polymerization reaction process cannot be observed by experiments.

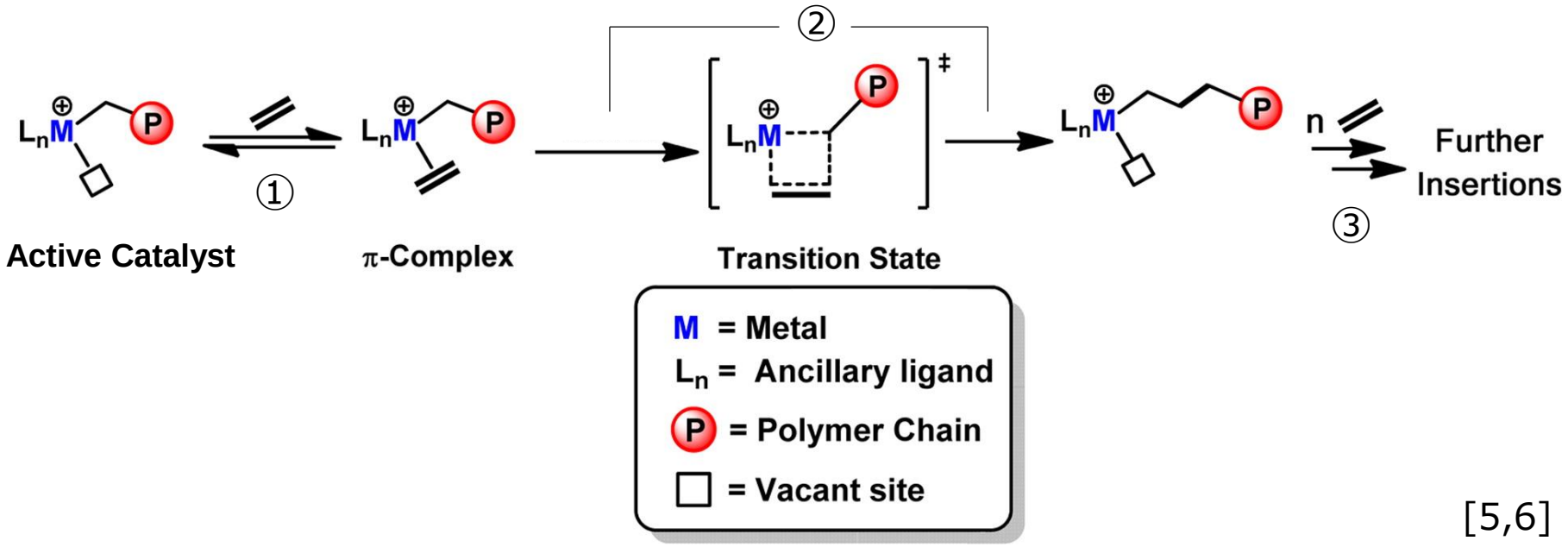
By using Red Moon (RM) method, we can observe the instantaneous and microscopic changes by polymerization reaction from an initial state to the final one.

[4] Sandhya, K. S.; Koga, N.; Nagaoka, M. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1093.

Purpose

To reproduce the polymerization reaction catalyzed by (1) using RM method

α-Olefin Polymerization Reaction by Catalyst

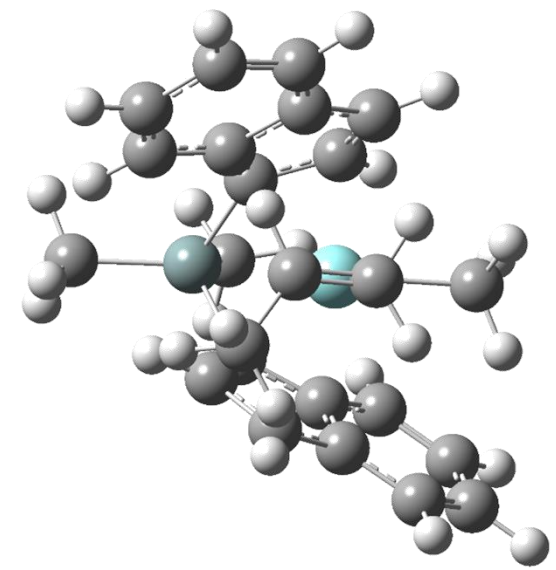


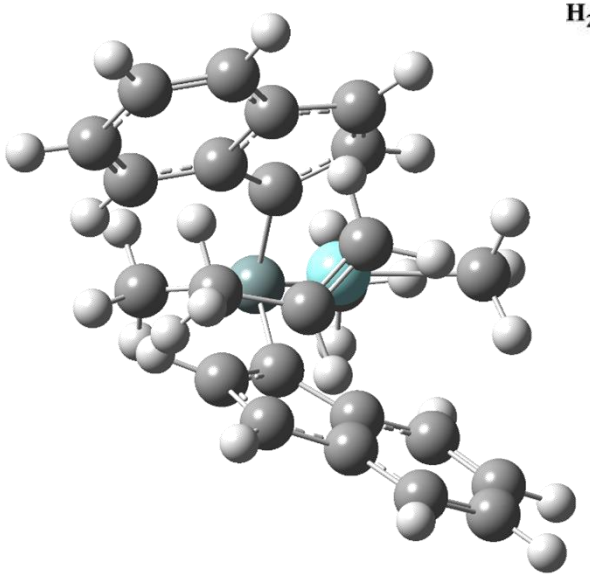
[5,6]

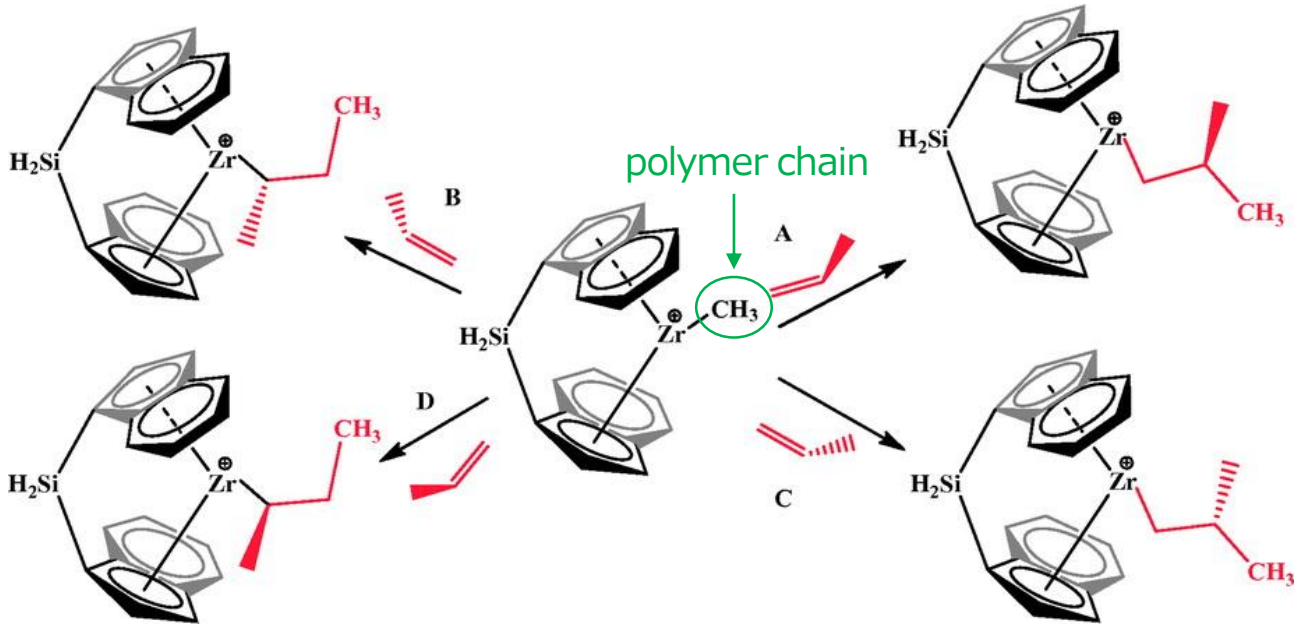
① coordination of the monomer (olefin) to the catalyst
② insertion of the olefin into the metal–alkyl bond
③ repetition of step ②

[5] Motta, A.; Fragalà, I. L.; Marks, T. J. *J. Chem. Theory Comput.* **2013**, *9*, 3491.
[6] Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

Coordination Patterns of Propylene



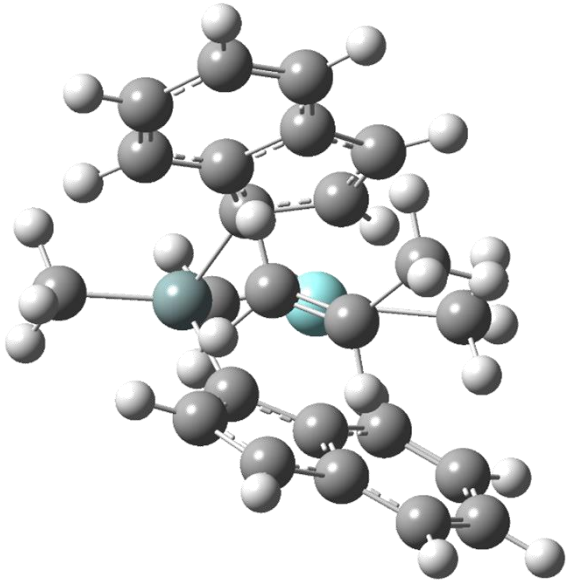


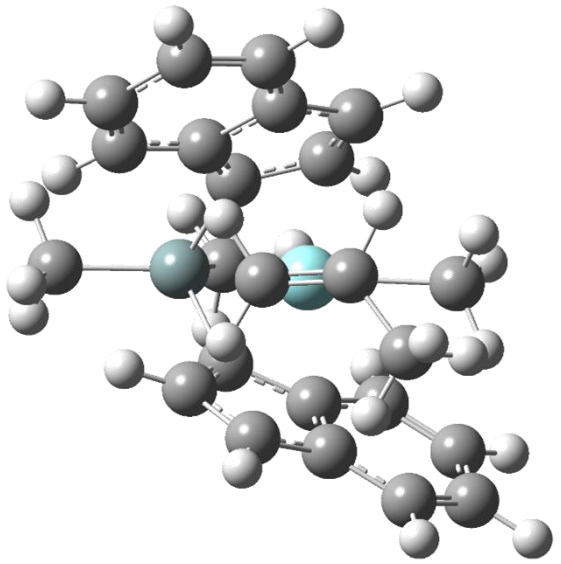


[4]

2,1-insertion (B and D)

1,2-insertion (A and C)

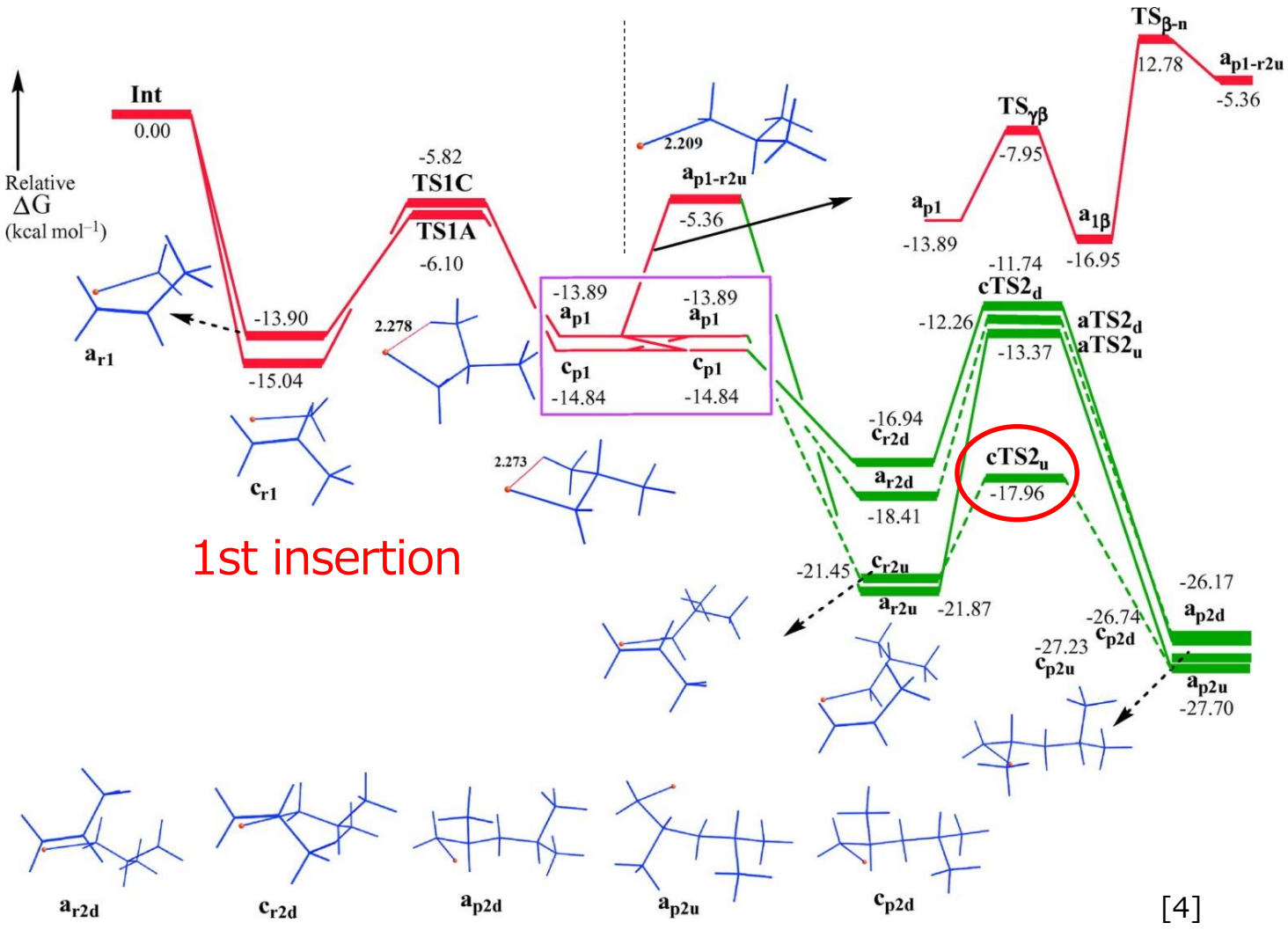




1,2-insertion is preferentially occurred.
→ **Only 1,2-insertion is considered.**

[4] Sandhya, K. S.; Koga, N.; Nagaoka, M. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1093.

Coordination Patterns of Propylene



[4]

1st insertion: 2 patterns (A and C)
- Orientation of CH_3 of propylene
  - A: up
  - C: down

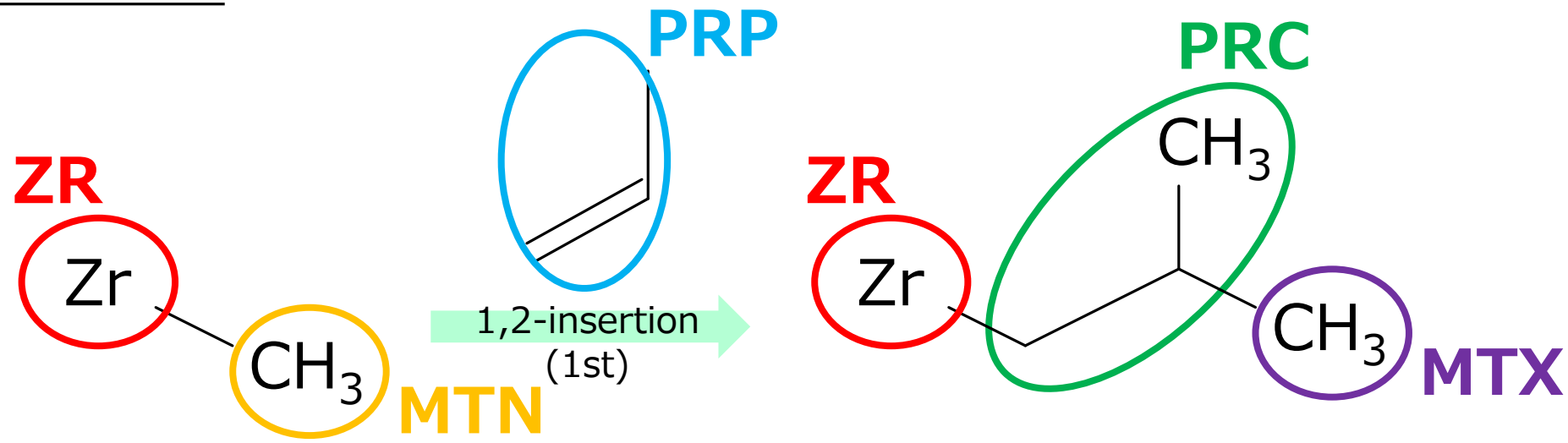
2nd and after 2nd insertions:
- 4 patterns (A-u, A-d, C-u, and C-d)
- Projection of growing polymer chain
  - u: up
  - d: down

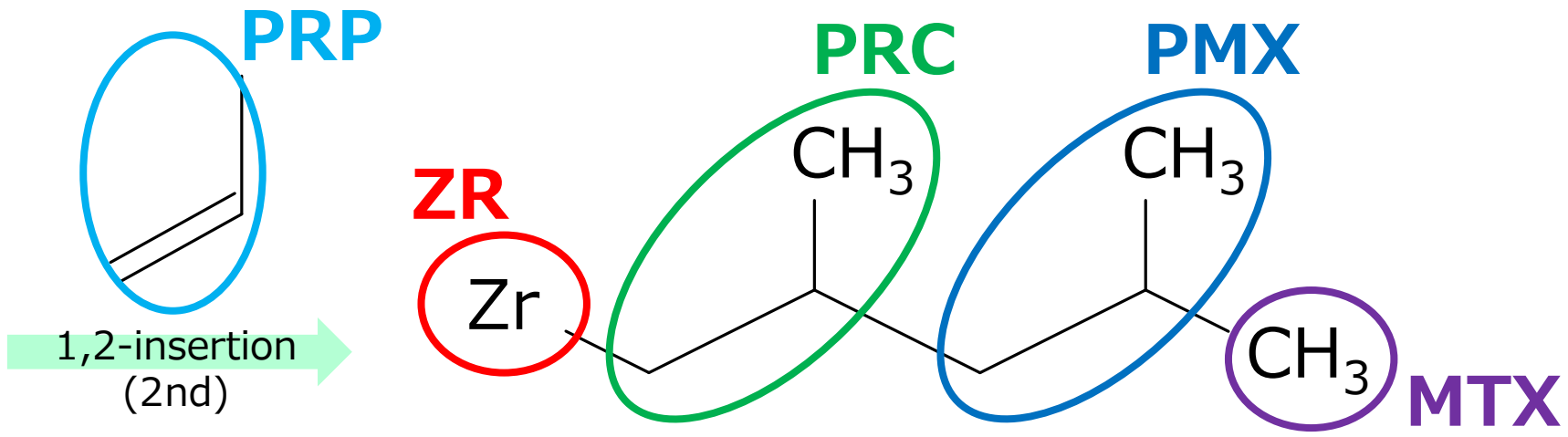
C-u is the most favorable pathway.

[4] Sandhya, K. S.; Koga, N.; Nagaoka, M. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1093.

Reaction Conditions

Residue Name

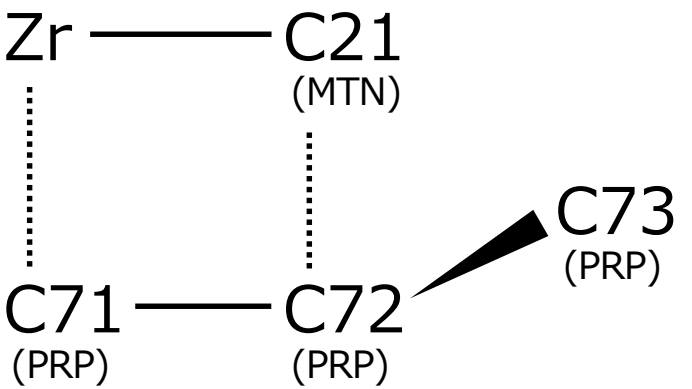




Reaction Conditions

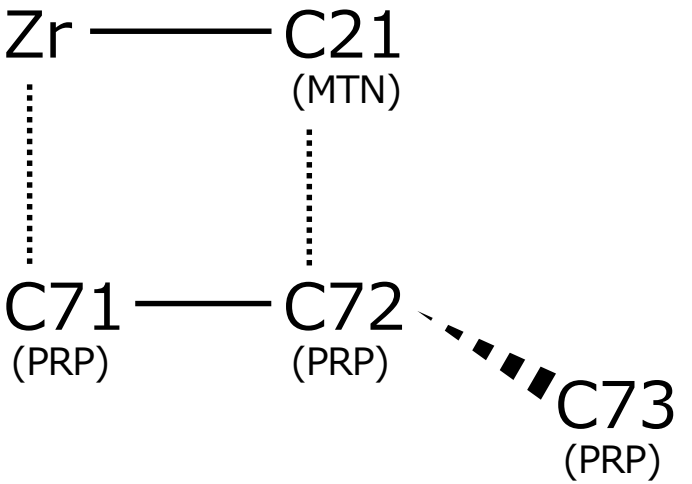
①1st insertion A: ReactID=1, Ea=7.80, dE=0.01

r(Zr–C71) < 3.8 Å;
r(Zr–C72) < 3.8 Å;
r(C21–C72) < 5.0 Å;
−90° ≤ *φ*(C21–Zr–C71–C72) ≤ 90°;
0° ≤ *φ*(Zr–C71–C72–C73) ≤ 180°



②1st insertion C: ReactID=2, Ea=9.22, dE=0.20

r(Zr–C71) < 3.8 Å;
r(Zr–C72) < 3.8 Å;
r(C21–C72) < 5.0 Å;
−90° ≤ *φ*(C21–Zr–C71–C72) ≤ 90°;
−180° ≤ *φ*(Zr–C71–C72–C73) ≤ 0°

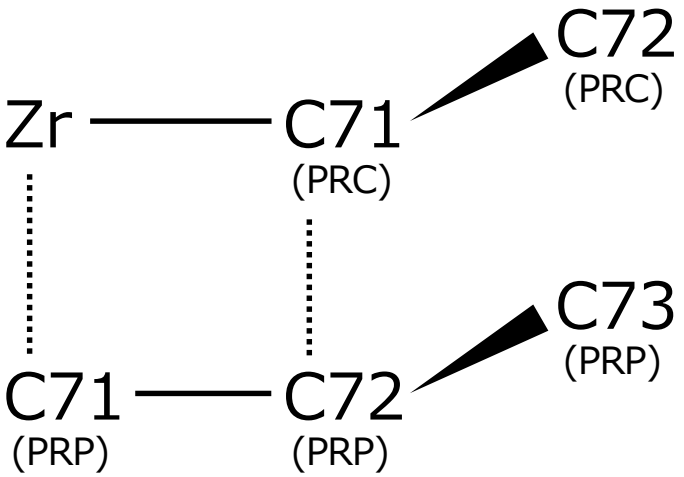


Ea: activation barrier, dE: reaction energy

Reaction Conditions

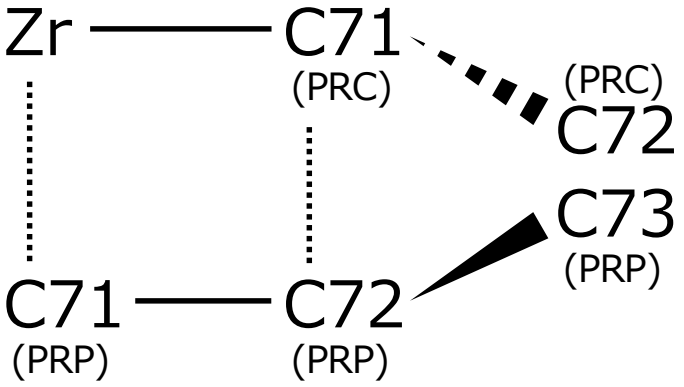
③2nd and after 2nd insertions A-u: ReactID=3, Ea=8.50, dE=−5.83

r(Zr–C71(PRP)) < 3.8 Å;
r(Zr–C72(PRP)) < 3.8 Å;
r(C71(PRC)–C72(PRP)) < 5.0 Å;
−90° ≤ *φ*(C71(PRC)–Zr–C71(PRP)–C72(PRP)) ≤ 90°;
0° ≤ *φ*(Zr–C71(PRP)–C72(PRP)–C73(PRP)) ≤ 180°;
−180° ≤ *φ*(C71(PRP)–Zr–C71(PRC)–C72(PRC)) ≤ 0°



④2nd and after 2nd insertions A-d: ReactID=4, Ea=6.15, dE=−7.76

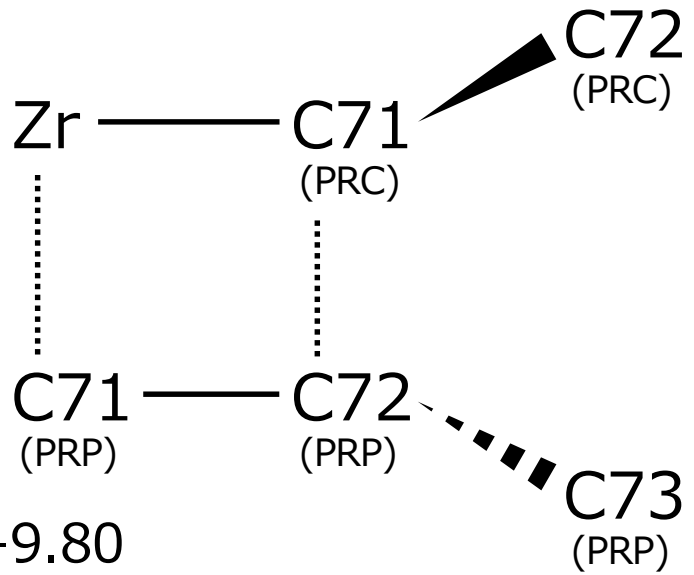
r(Zr–C71(PRP)) < 3.8 Å;
r(Zr–C72(PRP)) < 3.8 Å;
r(C71(PRC)–C72(PRP)) < 5.0 Å;
−90° ≤ *φ*(C71(PRC)–Zr–C71(PRP)–C72(PRP)) ≤ 90°;
0° ≤ *φ*(Zr–C71(PRP)–C72(PRP)–C73(PRP)) ≤ 180°;
0° ≤ *φ*(C71(PRP)–Zr–C71(PRC)–C72(PRC)) ≤ 180°



Reaction Conditions

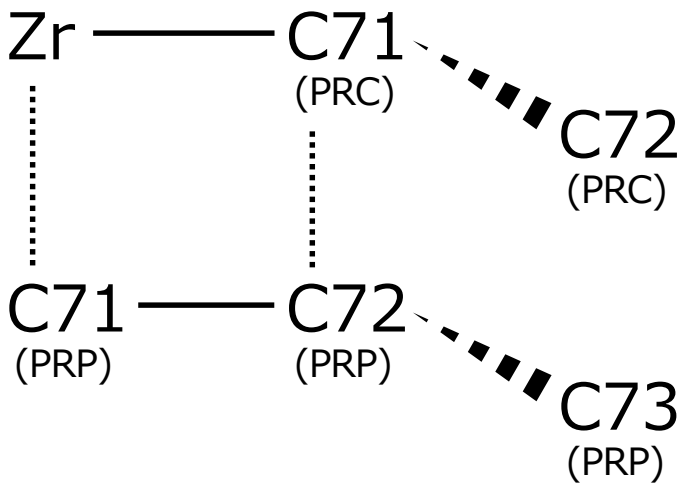
⑤2nd and after 2nd insertions C-u: ReactID=5, Ea=3.49, dE=−5.78 **most favorable pathway**

r(Zr–C71(PRP)) < 3.8 Å;
r(Zr–C72(PRP)) < 3.8 Å;
r(C71(PRC)–C72(PRP)) < 5.0 Å;
−90° ≤ *φ*(C71(PRC)–Zr–C71(PRP)–C72(PRP)) ≤ 90°;
−180° ≤ *φ*(Zr–C71(PRP)–C72(PRP)–C73(PRP)) ≤ 0°;
−180° ≤ *φ*(C71(PRP)–Zr–C71(PRC)–C72(PRC)) ≤ 0°



⑥2nd and after 2nd insertions C-d: ReactID=6, Ea=5.20, dE=−9.80

r(Zr–C71(PRP)) < 3.8 Å;
r(Zr–C72(PRP)) < 3.8 Å;
r(C71(PRC)–C72(PRP)) < 5.0 Å;
−90° ≤ *φ*(C71(PRC)–Zr–C71(PRP)–C72(PRP)) ≤ 90°;
−180° ≤ *φ*(Zr–C71(PRP)–C72(PRP)–C73(PRP)) ≤ 0°;
0° ≤ *φ*(C71(PRP)–Zr–C71(PRC)–C72(PRC)) ≤ 180°

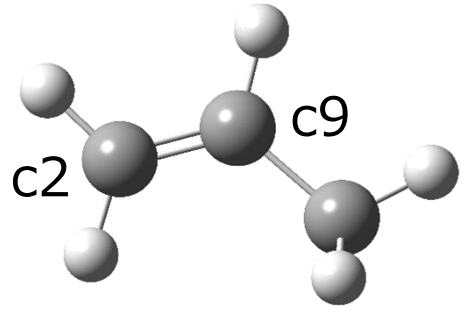


Computational Details

All MD calculations were performed by PMEMD in AMBER14.
Periodic boundary condition was applied.
SHAKE algorithm was used.

RM simulation was performed in NVT ensemble at 300 K.
Search MD: 50 ps
Configurations were sampled every 0.5 ps (100 snapshots).

To correctly represent the cation–counteranion and cation–propylene interactions, I modified the Lennard-Jones (LJ) parameters based on the QM calculations.



LJ Parameters for the Cation–Counteranion and Cation–Propylene Interactions

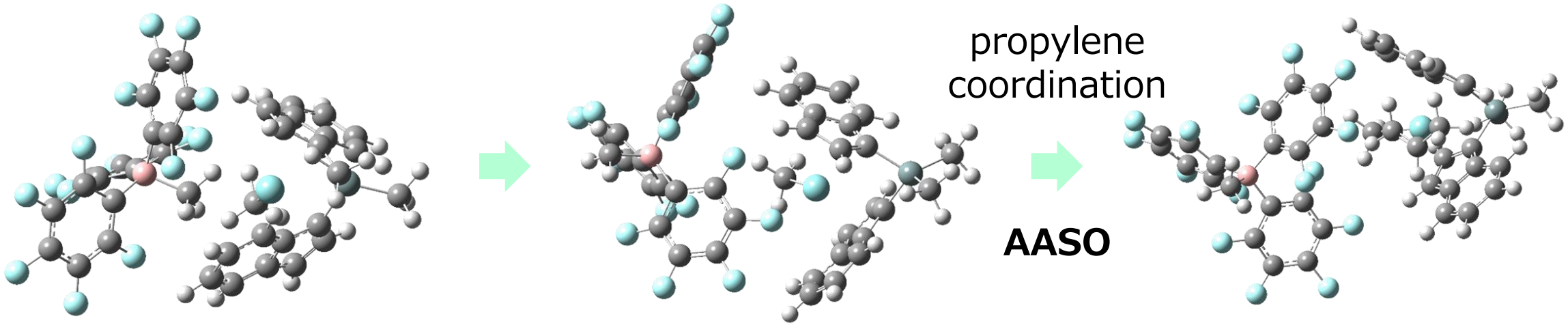
	ε [kcal mol^{-1}]	r^e [Å]
Zr–H(CH_3)	0.300	2.600
Zr–F	0.500	2.980

	ε [kcal mol^{-1}]	r^e [Å]
Zr–C(c2)	1.842	2.304
Zr–C(c9)	2.276	2.848

Red Moon Simulation

I executed the RM simulation
(System: 1 ion-pair, 120 propylene, and 480 solvent pentane).
→ Reaction candidates were **never** appeared.

<u>1.4 μs MD Simulation</u>



CH_3 group coordination

F atom(s) coordination

propylene coordination

The associative active site opening (AASO) occurs **only once**.

Red Moon Simulation

Either A or C was observed.
→ Sampling in Search MD is insufficient.

System: 1 cation, 120 propylene, and 480 solvent pentane

				React. Candidate
Cycle	3	ReactID	1 ..... Accepted	A	Only A
Cycle	4	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	6	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	11	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	22	ReactID	4 ..... Accepted	A-d	Only A
Cycle	30	ReactID	3 ..... Accepted	A-u	Only A
Cycle	31	ReactID	3 ..... Accepted	A-u	Only A
Cycle	33	ReactID	4 ..... Accepted	A-d	Only A
Cycle	35	ReactID	4 ..... Accepted	A-d	Only A
Cycle	36	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	46	ReactID	4 ..... Accepted	A-d	Only A
Cycle	47	ReactID	3 ..... Accepted	A-u	Only A
Cycle	48	ReactID	5 ..... Accepted	**C-u**	**Both A and C**
Cycle	51	ReactID	6 ..... Accepted	C-d	Only C
Cycle	53	ReactID	3 ..... Accepted	A-u	Only A
Cycle	60	ReactID	4 ..... Accepted	A-d	Only A
Cycle	61	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	63	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	64	ReactID	6 ..... Accepted	C-d	Only C
Cycle	67	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	77	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	78	ReactID	3 ..... Accepted	A-u	Only A
Cycle	79	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	82	ReactID	3 ..... Accepted	A-u	Only A

				React. Candidate
Cycle	110	ReactID	3 ..... Accepted	A-u	Only A
Cycle	118	ReactID	3 ..... Accepted	A-u	Only A
Cycle	121	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	124	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	183	ReactID	3 ..... Accepted	A-u	Only A
Cycle	232	ReactID	3 ..... Accepted	A-u	Only A
Cycle	335	ReactID	4 ..... Accepted	A-d	Only A
Cycle	337	ReactID	4 ..... Accepted	A-d	Only A
Cycle	341	ReactID	4 ..... Accepted	A-d	Only A
Cycle	344	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	348	ReactID	3 ..... Accepted	A-u	Only A
Cycle	349	ReactID	3 ..... Accepted	A-u	Only A
Cycle	354	ReactID	6 ..... Accepted	C-d	Only C
Cycle	355	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	357	ReactID	3 ..... Accepted	A-u	Only A
Cycle	362	ReactID	4 ..... Accepted	A-d	Only A
Cycle	363	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	364	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	365	ReactID	3 ..... Accepted	A-u	Only A
Cycle	367	ReactID	5 ..... Accepted	**C-u**	Only C
Cycle	376	ReactID	4 ..... Accepted	A-d	Only A
Cycle	378	ReactID	6 ..... Accepted	C-d	Only C
Cycle	383	ReactID	3 ..... Accepted	A-u	Only A
Cycle	386	ReactID	4 ..... Accepted	A-d	Only A

Red Moon Simulation

Once propylene coordinates to Zr, the π-complex hardly dissociates.

It is preferable that the number of the reaction candidates of A and C are almost same.

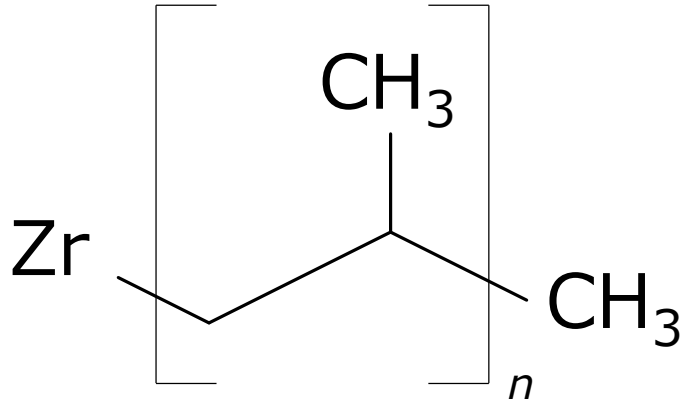
To solve this problem, **I optimized the LJ parameter, ε, of Zr–C(sp^2).**

Optimization of ε

System:

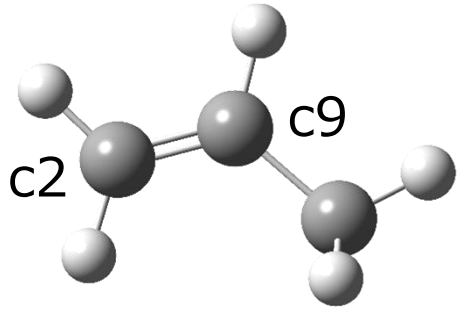
1 cation (n = 1, 2), (120 − n) propylene, and 480 solvent pentane

(n: the number of the inserted propylene)



[kcal mol^{-1}]

	Zr–C(c2)	Zr–C(c9)
ε	1.842	2.276
0.33ε	0.614	0.759
0.50ε	0.921	1.138
0.55ε	1.013	1.252
0.60ε	1.105	1.366
0.66ε	1.228	1.517



10 MD simulations for 5 ns were performed (total: 50 ns).
The average of the number of the reaction candidates per 1 ns were obtained.

Optimization of ε

$n = 1$

		React ID			
		3 (A-u)	4 (A-d)	5 (C-u)	6 (C-d)
0.33ε	ave.	2.4	4.2	3.3	4.2
	ratio	0.720	1.287	1.000	1.274
0.50ε	ave.	43.5	33.5	46.7	41.7
	ratio	0.932	0.717	1.000	0.894
0.55ε	ave.	93.4	77.8	105.5	70.0
	ratio	0.885	0.738	1.000	0.664
0.60ε	ave.	172.4	133.8	203.8	116.8
	ratio	0.846	0.657	1.000	0.573
0.66ε	ave.	269.4	185.5	322.8	173.3
	ratio	0.835	0.575	1.000	0.537

← Very small

← Balance is better.

ave.: average; 5 (C-u) was set to the reference (1.000).
Configurations were sampled every 0.5 ps (2000 snapshots).

Optimization of ε

$n = 2$

		React ID			
		3 (A-u)	4 (A-d)	5 (C-u)	6 (C-d)
0.33ε	ave.	2.0	0.2	2.1	0.6
	ratio	0.971	0.087	1.000	0.269
0.50ε	ave.	21.4	6.9	23.8	7.4
	ratio	0.899	0.291	1.000	0.309
0.55ε	ave.	32.8	10.8	42.4	13.0
	ratio	0.774	0.255	1.000	0.307
0.60ε	ave.	78.9	28.6	124.1	38.3
	ratio	0.636	0.231	1.000	0.309
0.66ε	ave.	185.1	43.8	264.1	39.5
	ratio	0.701	0.166	1.000	0.149

← Very small

← Balance is better.

0.50ε is a better choice.

ave.: average; 5 (C-u) was set to the reference (1.000).
Configurations were sampled every 0.5 ps (2000 snapshots).

Red Moon Simulation

System: 1 cation, 120 propylene, and 480 solvent pentane; Search MD: 1 ns

Cycle	1	ReactID 1 ..... Accepted	A
Cycle	4	ReactID 5 ..... Accepted	**C-u**
Cycle	11	ReactID 5 ..... Accepted	**C-u**
Cycle	13	ReactID 5 ..... Accepted	**C-u**
Cycle	17	ReactID 5 ..... Accepted	**C-u**
Cycle	18	ReactID 5 ..... Accepted	**C-u**
Cycle	21	ReactID 5 ..... Accepted	**C-u**
Cycle	22	ReactID 5 ..... Accepted	**C-u**
Cycle	23	ReactID 5 ..... Accepted	**C-u**
Cycle	26	ReactID 5 ..... Accepted	**C-u**
Cycle	28	ReactID 5 ..... Accepted	**C-u**
Cycle	29	ReactID 5 ..... Accepted	**C-u**
Cycle	31	ReactID 5 ..... Accepted	**C-u**
Cycle	32	ReactID 5 ..... Accepted	**C-u**
Cycle	38	ReactID 5 ..... Accepted	**C-u**
Cycle	41	ReactID 5 ..... Accepted	**C-u**
Cycle	42	ReactID 5 ..... Accepted	**C-u**
Cycle	43	ReactID 5 ..... Accepted	**C-u**
Cycle	48	ReactID 5 ..... Accepted	**C-u**
Cycle	55	ReactID 5 ..... Accepted	**C-u**
Cycle	56	ReactID 5 ..... Accepted	**C-u**
Cycle	61	ReactID 3 ..... Accepted	A-u
Cycle	65	ReactID 5 ..... Accepted	**C-u**
Cycle	67	ReactID 5 ..... Accepted	**C-u**
Cycle	80	ReactID 6 ..... Accepted	C-d
Cycle	81	ReactID 5 ..... Accepted	**C-u**
Cycle	82	ReactID 5 ..... Accepted	**C-u**
Cycle	85	ReactID 5 ..... Accepted	**C-u**
Cycle	88	ReactID 5 ..... Accepted	**C-u**
Cycle	91	ReactID 5 ..... Accepted	**C-u**
Cycle	95	ReactID 3 ..... Accepted	A-u
Cycle	96	ReactID 5 ..... Accepted	**C-u**
Cycle	98	ReactID 4 ..... Accepted	A-d
Cycle	103	ReactID 4 ..... Accepted	A-d
Cycle	105	ReactID 5 ..... Accepted	**C-u**
Cycle	108	ReactID 5 ..... Accepted	**C-u**
Cycle	109	ReactID 5 ..... Accepted	**C-u**
Cycle	112	ReactID 5 ..... Accepted	**C-u**
Cycle	115	ReactID 5 ..... Accepted	**C-u**
Cycle	116	ReactID 3 ..... Accepted	A-u
Cycle	117	ReactID 5 ..... Accepted	**C-u**
Cycle	119	ReactID 5 ..... Accepted	**C-u**
Cycle	126	ReactID 5 ..... Accepted	**C-u**
Cycle	127	ReactID 5 ..... Accepted	**C-u**
Cycle	132	ReactID 5 ..... Accepted	**C-u**
Cycle	133	ReactID 6 ..... Accepted	C-d
Cycle	135	ReactID 5 ..... Accepted	**C-u**
Cycle	137	ReactID 5 ..... Accepted	**C-u**

Summary and Conclusions

To reproduce the polymerization reaction catalyzed by (1) using RM method

- Reaction conditions were established for RM simulation.
- LJ parameters, ε, was optimized for proper sampling in Search MD.
- RM simulation of without-counteranion system is now in progress.

Perspective

- I will perform RM simulation of **with**-counteranion system.
  → Modification of LJ parameters between cation and counteranion will be needed.